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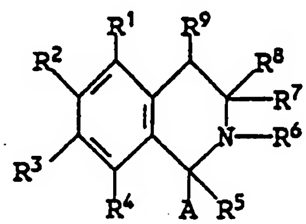

(I)

(57) Abstract

The invention provides a method of combating fungus at a locus which comprises treating the locus with a compound of general formula (I), or an N-alkyl or N-phenyl halide or N-oxide thereof, in which R^1, R^2, R^3 and R^4 independently represent a hydrogen or halogen atom, a hydroxyl group or an optionally substituted alkyl or alkoxy group, or R^1 and R^2 or R^2 and R^3 or R^3 and R^4 together with the interjacent carbon atoms represent a 5- to 7-membered saturated or unsaturated carbocyclic or heterocyclic ring in which a heterocyclic ring contains 1 to 3 heteroatoms selected from nigrogen, oxygen and sulphur atoms; R^5 represents a hydrogen or halogen atom, R^6 represents a hydrogen atom, or R^5 and R^6 together represent a single carbon-carbon bond; R^7 represents a hydrogen or halogen atom, an alkyl or alkoxy group optionally substituted by one or more halogen atoms, or an optionally substituted phenyl or phenoxy group; R^8 and R^9 independently represent a hydrogen atom or together represent a single carbon-carbon bond; and A represents an optionally substituted phenyl group. Certain of the isoquinoline derivatives are novel and a process for the preparation of these compounds and compositions containing them are also provided.

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FUNGICIDAL ISOQUINOLINE DERIVATIVES

The present invention relates to a method of combating fungi, especially phytopathogenic fungi, utilising certain isoquinoline derivatives, some of which are novel, a process for their preparation and compositions containing such compounds.

US 4717724 discloses compounds of the formula

$$G\text{-}CH_2\text{-}O\text{-}D \qquad (A)$$

in which G represents a 2-aryl-2-(1H-imidazol-1-yl-methyl)-1,3-dioxolan-4-ylmethyloxy or 2-aryl-2-(1,2,4-triazol-1-ylmethyl)-1,3-dioxolan-4-ylmethyloxy group and D represents an isoquinolin-6-yl, 3,4-dihydro-isoquinolin-6-yl or 1,2,3,4-tetrahydroisoquinolin-6-yl group. These compounds are said to be chemotherapeutic agents with activity against certain skin fungi, mold fungi, yeasts and bacteria. However, there is no suggestion of any activity against phytopathogenic fungi.

EP 0170524 A2 discloses isoquinolines and 3,4-dihydroisoquinolines substituted at the 1-position by a group $-C(R^A)=C(R^BR^C)$ in which R^A represents hydrogen or fluorine, R^B represents hydrogen, halogen, cyano, nitro or C_{1-2} alkyl optionally substituted by one or more halogen atoms, and R^C represents a group $-(CH=CH)_nR^D$ where n is 0-2 and R^D represents hydrogen,

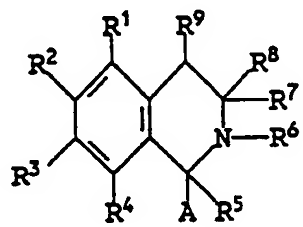
C_{1-8} alkyl, C_{2-8} alkenyl, C_{2-8} alkynyl or a monocyclic, bicyclic, tricyclic or tetracyclic ring system containing between three and sixteen ring members, optionally substituted by hydroxy, thio, halogen, fluorosulphonyl, nitro, cyano, C_{1-12} hydrocarbyl, C_{1-12}hydrocarbyloxy, C_{1-12} hydrocarbylthio wherein the said hydrocarbyl, hydrocarbyloxy and hydrocarbylthio groups are each optionally further substituted by halogen, hydroxy, thio, C_{1-2} alkylthio or C_{1-2} alkoxy groups, the groups R^B and R^C optionally being linked through a C_{1-4} alkylene bridge. These compounds are said to possess broad spectrum antifungal activity against fungi pathogenic in man, animals and plants. However, no evidence of activity against phytopathogenic fungi is provided.

EP 0251361 A1 discloses di- and tetrahydroisoquinoline derivatives substituted, inter alia, at the 1-position by an optionally substituted phenyl group and at the 3-position by substituents R^E and R^F whre R^E is hydrogen or a group $-CO-OR^G$ in which R^G is C_{1-4} alkyl, or R^E is a group $-CON(R^H)_2$ in which both groups R^H independently represent hydrogen or C_{1-4} alkyl, or R^E is a group $-CH_2OR^J$ in which R^J is hydrogen, C_{1-4} alkyl, tetrahydropyranyl, C_{1-4} alkanoyl, or carbamoyl optionally substituted by 1 or 2 C_{1-4} alkyl groups, and R^F is hydrogen or methyl. However, only one compound is specifically disclosed in which both R^E and R^F are hydrogen and that is 6,7-methylenedioxy-1-(3,4,5-trimethoxyphenyl)tetrahydroisoquinoline. The compounds are described as cytostatic agents, that is, they have antitumour activity.

It has now been discovered that certain isoquinoline derivatives exhibit good activity against

certain phytopathogenic fungi, particularly against fungi of the <u>Erysiphe</u> genus and, especially, powdery mildews in cereals.

According to the present invention there is therefore provided a method of combating fungus at a locus which comprises treating the locus with a compound of the general formula.



(I)

or an N-alkyl or N-phenyl halide or N-oxide thereof, in which

R^1, R^2, R^3 and R^4 independently represent a hydrogen or halogen atom, a hydroxyl group or an optionally substituted alkyl or alkoxy group, or R^1 and R^2 or R^2 and R^3 or R^3 and R^4 together with the interjacent carbon atoms represent a 5- to 7-membered saturated or unsaturated carbocyclic or heterocyclic ring in which a heterocyclic ring contains 1 to 3 heteroatoms selected from nitrogen, oxygen and sulphur atoms;

R^5 represents a hydrogen or halogen atom,

R^6 represents a hydrogen atom, or

R^5 and R^6 together represent a single carbon- carbon bond;

R^7 represents a hydrogen or halogen atom, an alkyl or alkoxy group optionally substituted by one or more halogen atoms or an optionally substituted phenyl or phenoxy group;

R^8 and R^9 independently represent a hydrogen atom or together represent a single carbon-carbon bond; and

A represents an optionally substituted phenyl group.

When the compounds of formula I contain an alkyl substituent group, this may be linear or branched and may contain up to 12, preferably up to 6, and especially up to 4, carbon atoms. An aralkyl group may be any alkyl group substituted by an aryl group, especially a benzyl group. A 5- to 7-membered saturated or unsaturated carbocyclic ring may be any 5- to 7-membered ring composed solely of carbon and hydrogen atoms, such as a cycloalkyl, cycloalkenyl, cycloalkynyl or cycloalkadienyl ring, with 5- and 6-membered rings being especially preferred. Examples of 5- to 7-membered saturated or unsaturated heterocyclic rings include tetrahydrofuran, furan, tetrahydrothiophene, thiophene, pyrrolidine, pyrrole, pyrroline, pyrazole, imidazole, triazole, pyrazoline, oxazole, thiazole, isoxazole, isothiazole, pyran, dihydropyran, tetrahydropyran, thiopyran, dihydrothiopyran, tetrahydrothiopyran, pyridine, piperidine, pyridazine, dihydropyridazine, tetrahydropyridazine, pyrimidine, dihydropyrimidine, tetrahydropyrimidine, pyrazine, dihydropyrazine, tetrahydropyrazine, morpholine, thiazine, dihydrothiazine, tetrahydrothiazine, piperazine and triazine.

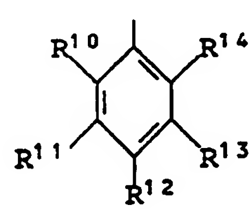
When any of the foregoing substituents are designated as being optionally substituted, the substituent groups which are optionally present may be any one or more of those customarily employed in the development of pesticidal compounds and/or the modification of such compounds to influence their structure/activity, persistence, penetration or other property. Specific examples of such substituents include, for example, halogen atoms, nitro, cyano, hydroxyl, cycloalkyl, alkyl, haloalkyl, alkoxy,

haloalkoxy, amino, alkylamino, dialkylamino, formyl, alkoxycarbonyl, carboxyl, alkanoyl, alkylthio, alkylsulphinyl, alkylsulphonyl, aralkyl, phenyl, phenoxy, pyridyl, carbamoyl and alkylamido groups. These optional substituents may themselves be optionally substituted, for instance, by one or more halogen atoms. When any of the foregoing substituents represents or contains an alkyl group, this may be linear or branched and may contain up to 12, preferably up to 6, and especially up to 4, carbon atoms.

It is preferred that R^1, R^2, R^3 and R^4 independently represent a hydrogen or halogen atom, a hydroxyl group or a C_{1-6} alkyl or C_{1-6} alkoxy group each optionally substituted by one or more halogen atoms or C_{1-4} alkoxy groups, or R^1 and R^2 or R^2 and R^3 or R^3 and R^4 together with the interjacent carbon atoms represents a 5- or 6-membered saturated heterocyclic ring containing two oxygen atoms especially a dioxane or dioxolane ring.

It is also preferred that R^7 represents a hydrogen atom or a C_{1-6} alkyl, especially C_{1-4} alkyl, group.

Preferably, A represents a group



in which
R^{10}, R^{11}, R^{12}, R^{13} and R^{14} independently represent a

hydrogen or halogen atom, a hydroxyl, nitro or amino group, or an optionally substituted alkyl, alkoxy, alkylamino, dialkylamino, alkylthio, alkylsulphinyl, alkylsulphonyl, aralkyl, phenyl, phenoxy or pyridyl group.

More preferably, R^{10}, R^{11}, R^{12}, R^{13} and R^{14} independently represent a hydrogen or halogen atom, a hydroxyl, nitro or amino group, or an alkyl, alkoxy, alkylsulphonyl, benzyl, phenyl, phenoxy or pyridyl group each optionally substituted by one or more halogen atoms.

A particularly preferred sub-group of compounds is that in which R^1, R^2, R^3 and R^4 independently represent a hydrogen, chlorine or bromine atom or a hydroxyl, methyl, ethyl, propyl, methoxy, ethoxy, propoxy, butoxy, pentyloxy, hexyloxy or methoxyethoxy group, or R^2 and R^3 together with the interjacent carbon atoms represent a 1,3-dioxolane ring; R^5 represents a hydrogen or chlorine atom, R^6 represents a hydrogen atom, or R^5 and R^6 together represent a single carbon-carbon bond; R^7 represents a hydrogen atom or an ethyl group; and R^{10}, R^{11}, R^{12}, R^{13} and R^{14} independently represent a hydrogen, fluorine, chlorine, bromine or iodine atom or a hydroxyl, nitro, amino, methyl, trifluoromethyl, methoxy, methylsulphonyl, benzyl, phenyl, phenoxy or chloropyridyl group.

Preferably, the locus comprises plants subject to or subjected to fungal attack, seeds of such plants or the medium in which such plants are growing or are to be grown.

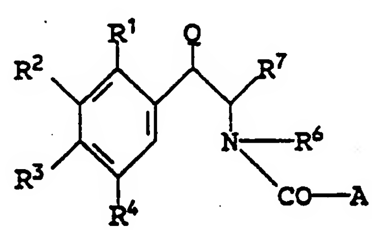
The present invention still further provides the use as a fungicide of a compound of the general formula I as defined above or an N-alkyl or N-phenyl halide or N-oxide thereof, preferably for the

treatment of fungal diseases in plants. In particular, the compounds according to general formula I may be advantageously used for the treatment of powdery mildew in plants, especially for the control of fungi of the Erysiphe genus.

Certain of the compounds of formula I are novel and the invention therefore also provides a compound of the general formula I or an N-alkyl or N-phenyl halide or N-oxide thereof as defined above with the proviso that, when R^1, R^4, R^5, R^6, R^7, R^8 and R^9 all represent a hydrogen atom and A represents a 3,4,5-trimethoxyphenyl group, then R^2 and R^3 together with the interjacent carbon atoms do not represent a 1,3-dioxolane ring.

The present invention also provides a process for the preparation of a compound of formula I as defined in the preceding paragraph or an N-alkyl or N-phenyl halide or N-oxide thereof which comprises

(a) cyclising a compound of the general formula



(II)

in which R^1, R^2, R^3, R^4, R^6, R^7 and A are as defined above and, when R^8 and R^9 in the resultant compound of formula I both represent a hydrogen atom then Q represents a hydrogen atom, and, when R^8 and R^9 in the resultant compound of formula I together represent a single carbon-carbon bond then Q represents an alkoxy, especially methoxy, group, in the presence of a

dehydrating agent to form a compound of formula I in which R^5 and R^6 together represent a single carbon-carbon bond;

followed, if desired, when R^8 and R^9 both represent a hydrogen atom, by

(b) hydrogenating the resulting compound of formula I to produce a compound of formula I in which R^5, R^6, R^8 and R^9 all represent a hydrogen atom; or

(c) dehydrogenating the resulting compound of formula I to produce a compound of formula I in which R^5 and R^6 together and R^8 and R^9 together both represent a single carbon-carbon bond;

followed, if desired, by

(d) oxidising the compound of formula I formed in (a), (b) or (c) to form an N-oxide thereof; or

(e) converting the compound of formula I formed in (a), (b) or (c) to the corresponding N-alkyl or N-phenyl halide.

The dehydrating agent used in step (a) may be selected from phosphorus oxychloride, phosphorus pentoxide, phosphorus pentachloride, polyphosphoric acid, aluminium chloride and thionyl chloride with phosphorus oxychloride being particularly pareferred. Preferably, the reaction is carried out in an inert solvent, such as chloroform, benzene, toluene, xylene, nitrobenzene or tetraline. Depending on the reactivity of the reactants, the reaction may be carried out under cooling, at room temperature or at elevated temperature up to the boiling point of the reaction mixture. Generally, this step is suitably carried out under reflux.

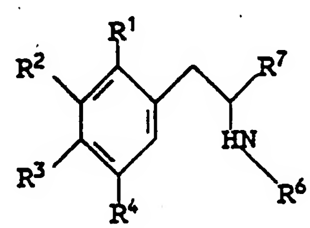
Preferably, the hydrogenation in step (b) is accomplished by catalytic hydrogenation, that is, by using hydrogen gas under elevated pressure in the presence of a catalyst preferably selected from the

platinum group of elements, such as platinum dioxide. This step is conveniently carried out at room temperature in the presence of an inert solvent, such as methanol or ethanol.

It is also preferred that the dehydrogenation in step (c) is accomplished by reaction with an oxidising agent, such as potassium permanganate used under acidic conditions or palladium on charcoal in the absence of hydrogen. This step may be conveniently carried out at a temperature from room temperature to the reflux temperature of the reaction mixture depending on the nature of the dehydrogenating agent used.

Preferably, the oxidising agent used in step (d) is a peracid, such as m-chloroperbenzoic acid. This step may be conveniently carried out at room temperature.

A compound of formula II in which Q represents a hydrogen atom may be conveniently prepared by the process of A. Bischler and B. Napieralski, Ber. dtsch. chem. Ges. 26, 1903 (1893) in which an amine of general formula III



(III)

wherein R^1, R^2, R^3, R^4, R^6 and R^7 are as hereinbefore defined is reacted with an acid derivative of general formula A-CO-X or A-CO-O-CO-A in which A is as hereinbefore defined and X is a bromine or chlorine atom.

Accordingly, an appropriately substitued β-aryl ethylamine is reacted with a substituted benzoic acid derivative, such as the acid chloride or anhydride, in an inert solvent, e.g. benzene, toluene, dichloromethane, or a promoting solvent, e.g. pyridine, lutidine, or in mixtures thereof. When inert solvents are used it is advantageous to add at least one equivalent of a tertiary amine, such as triethylamine, diisopropyl ethylamine or 2,4,6-collidine. Depending on the reactivity of the reactants, the reaction may be carried out under cooling, at room temperature or at elevated temperature up to the boiling point of the reaction mixture. Generally, the reaction takes place under cooling.

A compound of formula II in which Q represents an alkoxy group may be prepared according to C.U.F. Mannich and M. Falber, Arch. Pharm., 267, 601 (1929).

Compounds of formula III and the acid derivatives of formula A-CO-X and A-CO-O-CO-A are known compounds or can be prepared by processes analogous to known processes.

The invention also provides fungicidal compositions which comprise a carrier and, as active ingredient, at least one of the compounds according to general formula I, as well as procedures for control of phytopathogenic fungi.

The compounds according to general formula I may be used as such, however, they are preferably used as compositions comprising, besides the compounds according to the invention, adjuvants and auxiliaries which are known for formulation purposes and may be manufactured into e.g. emulsion concentrates, solutions which may be sprayed directly or diluted, diluted emulsions, wettable powders, soluble powders,

dusts, granulates, microencapsulates by well-established procedures. The form of application such as spraying, atomising, dispersing, pouring may be chosen, like the compositions, according to the desired objectives and the given circumstances.

The formulations, that is, the compositions which comprise at least one compound according to general formula I and optionally solid and/or liquid auxiliaries and adjuvants, may be prepared by well-established procedures, e.g. intensive mixing and/or grinding of the active ingredients with other substances, such as fillers, solvents, solid carriers, and optionally surface-active compounds (tensides). The composition may contain at least two carriers, at least one of which is a surface-active agent.

Solvents may be aromatic hydrocarbons, preferably the fractions C_8 to C_{12}, e.g. xylenes or xylene mixtures, substituted naphthalenes, phthalic acid esters, such as dibutyl or dioctyl phthalate, aliphatic hydrocarbons, e.g. cyclohexane or paraffins, alcohols and glycols as well as their ethers and esters, e.g. ethanol, ethyleneglycol mono- and dimethyl ether, ketones such as cyclohexanone, strongly polar solvents such as N-methyl 2-pyrrolidone, dimethyl sulphoxide, alkyl formamides, epoxidised vegetable oils, e.g. epoxidised coconut or soybean oil, water.

Solid carriers, which may be used for dusts or dispersible powders, may be mineral fillers, such as calcite, talc, kaolin, montmorillonite, attapulgite. The physical properties may be improved by addition of highly dispersed silica gel or highly dispersed polymers. Carriers for granulates may be porous material, e.g. pumice, broken brick, sepiolite, bentonite, non-sorptive carriers may be calcite or

sand. Additionally, a multitide of pre-granulated inorganic or organic materials may be used, such as dolomite or crushed plant residues.

Suitable surface-active substances may be non-ionogenic, anionic or cationic tensides with good dispersing, emulgating and wetting properties depending on the nature of the compound according to general formula I to be formulated. Tensides may also mean mixtures of tensides.

Suitable tensides may be so-called water-soluble soaps as well as water-soluble synthetic surface-active compounds.

Soaps usually are alkali, earth alkali or optionally-substituted ammonium salts of higher fatty acids (C_{10}-C_{20}), e.g. the sodium or potassium salts of oleic or stearic acid or of mixtures of natural fatty acids which are prepared, for example, from coconut or tallow oil. Furthermore, methyl-taurin salts of fatty acids may be used.

However, so-called synthetic tensides are preferably used, especially fatty sulphonates, fatty sulphates, sulphonated benzimidazole derivatives or alkyl aryl sulphonates.

The fatty sulphates or fatty sulphonates are normally used as alkali, earth alkali or optionally-substituted ammonium salts and have an alkyl moiety of 8 to 22 carbon atoms, whereby alkyl also means the alkyl moiety of acyl residues, such as the sodium or calcium salt of lignin sulphonic acid, of sulphuric acid dodecylate or of a mixture of fatty alcohols prepared from natural fatty acids. This also includes the salts of sulphuric acid esters, sulphonic acids and adducts of fatty alcohols and ethylene oxide. The sulphonated benzimidazole derivatives preferably contain 2 sulphonic acid residues and a

fatty acid residue with 8 to 22 carbon atoms. Alkyl aryl sulphonates are, for example, the sodium, calcium or triethyl ammonium salts of dodecyl benzene sulphonic acid, dibutyl naphthalene sulphonic acid or of a condensate of naphthalene sulphonic acid and formaldehyde.

Furthermore, phosphates, such as the salts of the phosphoric acid ester of a p-nonylphenol-(4-14)-ethylene oxide adduct or phospholipids, may be used.

Non-ionic tensides are preferably polyglycolether derivatives of aliphatic or cycloaliphatic alcohols, saturated or non-saturated fatty acids and alkylphenols, which have 3 to 10 glycol ether groups and 8 to 20 carbon atoms in the (aliphatic) hydrocarbon residue and 6 to 18 carbon atoms in the alkyl residue of the alkyl phenols.

Other suitable non-ionic tensides are the water-soluble, 20 to 250 ethylene glycol ether groups containing polyadducts of ethylene oxide and polypropylene glycol, ethylene diamino polypropylene glycol and alkyl polypropylene glycol with 1 to 10 carbon atoms in the alkyl moiety, the substances normally contain 1 to 5 ethylene glycol units per propylene glycol unit.

Examples of non-ionic tensides are nonylphenol polyethoxy ethanols, castor oil polyglycol ether, polyadducts of ethylene oxide and polypropylene, tributyl phenoxy polyethoxy ethanol, polyethylene glycol, octyl phenoxy polyethoxy ethanol.

Furthermore, fatty acid esters of polyoxy ethylene sorbitan, such as polyoxy ethylene sorbitan trioleate may be used.

Cationic tensides preferably are quarternary ammonium salts, which have at least one alkyl residue with 8 to 22 carbon atoms and, furthermore, low,

optionally-halogenated alkyl, benzyl or hydroxyalkyl residues. The salts are preferably halides, methyl sulphates or alkyl sulphates, e.g. stearyl trimethyl ammonium chloride or benzyl bis(2-chloroethyl) ethyl ammonium bromide.

The tensides generally used for compositions are disclosed in such publications as:

"McCutheon's Detergents and Emulsifiers Annual", MC Publishing Corp., Ridgewood, NJ, USA 1981;

H. Stache, "Tensid-Taschenbuch", 2nd ed., C. Hanser, Munich, Vienna, 1981;

M. and J. Ash, "Encyclopedia of Surfactants", vol. I-III, Chemical Publishing Co., New York, NY, USA 1980-1981.

The pesticidal compositions usually comprise 0.1% to 95%, preferably 0.1% to 80% of at least one compound according to general formula I, 1% to 99.9% of a solid or liquid adjuvant and 0% to 25%, preferably 0.1% to 25%, of a tenside.

The preferred compositions usually comprise.

As commodity, the compositions may preferably be in a concentrated form whereas the end-user generally employs diluted compositions. The compositions may be diluted to a concentration of 0.001% of active ingredient (a.i.). The doses usually are in the range from 0.01 to 10 kg. a.i./ha.

The compositions may also comprise other auxiliaries such as stabilisers, defoamer, viscosity controlling agents, thickeners, adhesives, fertilisers or other active ingredients to obtain special effects.

The present invention is further illustrated by the following examples. It should be understood, however, that the invention is not limited solely to the particular examples given below.

EXAMPLES

EXAMPLE 1

Preparation of 1-(4'-phenoxyphenyl)-6,7-dimethoxy-3,4-dihydroisoquinoline

$R^1=R^4=H$; $R^2=R^3=CH_3O$; R^5/R^6=single C-C bond; $R^7=R^8=R^9=H$; A=4-phenoxyphenyl)

(i) Preparation of N-[β-(3',4'-dimethoxyphenyl)-ethyl]-4-phenoxy benzoic acid amide

β-(3,4-Dimethoxyphenyl)ethylamine (3.9g, 21.5mmol) and triethylamine (2ml) were dissolved in dichloromethane (50ml). 4-Phenoxy benzoic acid chloride (5g, 20mmol), dissolved in dichloromethane (10ml), was added over a period of 10 minutes with stirring whilst maintaining the temperature of the mixture below 10°C. The stirring was continued for another 2 hours and the reaction mixture was then washed twice with water (50ml each), dried with magnesium sulphate

and evaporated. The residue was triturated with diisopropyl ether and the precipitate collected by vacuum filtration and dried. Off-white crystals of N-[β-(3',4'-dimethoxyphenyl)-ethyl]-4-phenoxy benzoic acid amide (7g, 88% of theoretical yield), m.pt. 118°C, were obtained.

(ii) Preparation of 1-(4'-phenoxyphenyl)-6,7-dimethoxy-3,4-dihydroisoquinoline

The N-[β-(3',4'-dimethoxyphenyl)ethyl]-4-phenoxy benzoic acid amide (6.5g, 18.1mmol) prepared in (i) above was dissolved in phosphorus oxychloride (50ml) and heated for 10 hours under reflux. The phosphorous oxychloride was then removed by vacuum distillation and the residue dissolved in water. The solution was made alkaline by addition of 2N aqueous sodium hydroxide and extracted several times with dichloromethane. The collected organic layers were dried with magnesium sulphate and the solvent was then evaporated *in vacuo*. Subsequent column chromatography on silica gel with dichloromethane/acetone (5:1) as eluant yielded 4g, 1-(4'-phenoxyphenyl)-6,7-dimethoxy-3,4-dihydroisoquinoline (66% of theoretical yield) as a viscous oil.

^{1}H-NMR:(ppm) δ= 2.76(t,2H), 3.77(s,3H), 3.80 (t,2H), 3.98(s,3H), 6.82(s,1H), 6.87(s,1H), 7.11(m,4H), 7.16 (t,1H), 7.41(t,2H), 7.62(d,2H)

EXAMPLE 2

Preparation of 1-(2',6'-difluorophenyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (R^1=R^4=H; R^2=R^3=CH_3O; R^5=R^6=R^7=R^8=R^9=H; A=2,6-difluorophenyl)

1-(2',6'-Difluorophenyl)-6,7-dimethoxy-3,4-dihydroisoquinoline (6.5g, 21.4mmol), prepared by a method analogous to Example 1, was dissolved in methanol. Platinum dioxide catalyst (0.7g) was added and the reaction mixture hydrogenated under a hydrogen pressure of 5bar for 3.5 hours at room temperature. The catalyst was then filtered off and the filtrate evaporated. The residue was applied onto a silica gel column and eluted with dichloromethane/acetone (10:1) to give 2g 1-(2',6'-difluorophenyl)-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (31% of theoretical; m.pt. 115°C), which crystallised on evaporation.

^{1}H-NMR:(ppm) δ= 2.71(d,1H), 2.97(m,1H), 3.10 (m,1H), 3.40 (m,1H), 3.64(s,3H), 3.86(s,3H), 5.50(s,1H), 6.18(s,1H), 6.60(s,1H), 6.90(t,2H), 7.25(m,1H)

EXAMPLE 3

Preparation of 1-(2-nitrophenyl)-5,6-dimethoxy-isoquinoline

(R^1=R^2=CH_3O; R^3=R^4=R^7=H; R^5/R^6=single C-C bond; R^7=H; R^8/R^9=single C-C bond; A=2-nitrophenyl)

N-(2-nitrobenzoyl)-2-methoxy-2-(2,3-dimethoxy-phenyl)ethylamine (4.4g, 0.012mol) prepared according to C.U.F. Mannich and M. Falber, Arch. Pharm. 267, 601 (1929)) was dissolved in phosphorus oxychloride (20ml) and heated under reflux for 2 hours. After cooling down, the reaction mixture was poured into water (200ml), the solution was made alkaline (pH8) by addition of sodium hydroxide and extracted 2-3 times with ethyl acetate (100ml each). The organic layers were collected, dried with anhydrous sodium sulphate and the solvent was evaporated *in vacuo*. The residual dark oil was applied onto a silica gel column (15cm x 3.5cm). Elution with petrol ether/ethyl acetate (3:1)

gave 2.76g 1-(2-nitrophenyl)-5,6-dimethoxy-isoquinoline, which crystallised as yellowish crystals, m.pt. 95°C, Yield: 73% of theoretical

^{1}H-NMR: δ= 4.01(s,3H), 4.02(s,3H), 7.35 (m,2H), 7.70(m,2H), 8.05(d,1H), 8.25(d,1H), 8.48ppm(d,1H)

EXAMPLE 4

Preparation of 1-(2-fluorophenyl)-6,7-dimethoxy-isoquinoline

(R^1=R^4=H; R^2=R^3=CH_3O; R^5/R^6=single C-C bond; R^7=H; R^8/R^9=single C-C bond; A=2-fluorophenyl)

1-(2-Fluorophenyl)-6,7-dimethoxy-3,4-dihydroisoquinoline (5.7g, 0.019 mol; prepared according to N.W. Whaley et al., Organic Reactions VI, 74 (1951)) was dissolved in a mixture of water (100ml) and conc. HCl and potassium permanganate (12.7g, 0.08mol) was added in several portions. The reaction mixture was stirred for another 4 hours, then the precipitated manganese dioxide was removed by filtration and the filter cake was washed with ethyl acetate (100ml). The filtrate was extracted three times with ethyl acetate (100ml each). All organic layers were collected, dried with anhydrous sodium sulphate and the solvent was evaporated in vacuo. The residual brownish oil was applied onto a silica gel column (15cm x 3.5cm) and eluted with petrol ether/ethyl acetate (3:1) to give 2.77g 1-(2-fluorophenyl)-6,7-dimethoxyisoquinoline as yellowish crystals, m.pt. 104°C, Yield: 40% of theoretical

^{1}H-NMR: δ= 3.83(s,3H), 4.04(s,3H), 7.00(s,1H), 7.35(m,6H), 8.45ppm (d,1H)

EXAMPLE 5

Preparation of 1-(2,6-difluorophenyl)-6,7-dimethoxy-isoquinoline

R^1=R^4=H; R^2=R^3=CH_3O;R^5/R^6=single C-C bond; R^7=H; R^8/R^9=single C-C bond; A=2,6-difluorophenyl)

1-(2,6-Difluorophenyl)-6,7-dimethoxy-3,4-dihydro-isoquinoline (6.5g, 0.021mol; prepared according to N.W. Whaley et al., Organic Reactions VI, 74 (1951)) was suspended in 60ml Decalin (Trade mark: decahydronaphthalene). Nitrobenzene (2.4g, 0.02mol) and palladium (10% on charcoal, 2.4g) were added. The reaction mixture was heated under reflux in a nitrogen atmosphere for 30 hours, then cooled down and the solvent evaporated *in vacuo*. The residue was taken up in dichloromethane (100ml) and filtered through silica gel. After evaporation of the solvent, the residue was applied onto a silica gel column (15cm x 3.5cm) and eluted with dichloromethane/acetone (10:1) to give 1.6g 1-(2,6-difluorophenyl)-6,7- dimethoxyisoquinoline as beige crystals, m.pt. 185°C. Yield: 25% of theoretical.

^{1}H-NMR: δ= 3.84(s,3H), 4.06(s,3H), 6.78 (s,1H), 7.09(m,3H), 7.44(m,1H), 7.62(d,1H), 8.55ppm (d,1H)

EXAMPLE 6

Preparation of 1-(2,6-Dichlorophenyl)-6-ethoxy-7-propoxyisoquinoline N-oxide:

R^1=R^4=H; R^2=C_2H_5O; R^3=C_3H_7O; R^5/R^6=single C-C bond; R^7=H; R^8/R^9=single C-C bond; A=2,6-difluorophenyl;N-oxide)

1-(2,6-Dichlorophenyl)-6-ethoxy-7-propoxy-isoquinoline (1.4g, 0.0037mol) prepared as described in any of Examples 3,4 and 5, and m-chloroperbenzoic acid (50%; 1.3g, 0.0037mol) in chloroform (20ml) were stirred at room temperatue for 2 hours. The reaction

mixture was then washed with dilute aqueous sodium carbonate and with water (50ml each), the organic layer was dried with sodium sulphate and the solvent was evaporated <u>in vacuo</u>. The remaining reddish oil (1.7g) was applied onto a silica gel column (3.5 x 15cm). Elution with acetone/ethyl acetate (1:4) gave a yellow oil (1.4g) which crystallised upon trituration with petrol ether to give 1.2g 1-(2,6-dichlorophenyl)-6-ethoxy-7-propoxyisoquinoline N-oxide, m.pt. 148°C, Yield: 82% of theoretical

^{1}H-NMR:(ppm) δ= 1.00(t,3H); 1.56(t,3H); 1.74-1.82(m,2H); 3.82(m,2H); 4.23 (m,2H); 6.35(s,1H); 7.10(s,1H); 7.37-7.66(m,4H); 8.30(d,1H)

<u>EXAMPLE 7</u>

<u>Preparation of 1-(2-nitrophenyl)-3,4-dihydro-6-ethoxy-7-propoxy- isoquinoline N-oxide:</u>
<u>(R^1=R^4=H;R^2=C_2H_5O; R^3=C_3H_7O; R^5/R^6=single C-C- bond; R^7=R^8=R^9=H; A=2=nitrophenyl; N-oxide)</u>

1-(2-Nitrophenyl)-3,4-dihydro-6-ethoxy-7-propoxy-isoquinoline (4.0g, 0.011mol), prepared as described in Example 1, and m-chloroperbenzoic acid (50%; 3.9g, 0.011mol) in chloroform (50ml) were stirred at room temperature for 2 hours. The reaction mixture was then washed with dilute aqueous sodium carbonate and with water (50ml each), the organic layer was dried with sodium sulphate and the solvent was evaporated <u>in vacuo</u>. The remaining orange-yellow oil (5.1g) was applied onto a silica gel column (3.5 x 15cm). Elution with acetone/ethyl acetate (1:4) gave 4.2g 1-(2-nitrophenyl)-3,4-dihydro-6-ethoxy-7-propoxy-isoquinoline-N-oxide as orange-yellow crystals, m.pt. 82-83°C. Yield: 100% of theoretical.

^{1}H-NMR:(ppm) δ=0.9(t,3H); 1.43(t,3H); 1.66(m,2H); 3.0-3.3(2m,2H); 4.1-4.2(m,2H); 6.2(s,1H); 6.25(s,1H); 7.5-8.2(m,4H)

EXAMPLES 8 TO 119

By processes similar to those described in Examples 1 to 7 above, further compounds according to the invention were prepared as detailed in Table 1 below. In this table, the compounds are identified by reference to formula I. Physical data and NMR spectroscopic data for the compounds of Examples 8 to 119 are given in Table IA below.

TABLE I

Example No.	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	A
8	H	H	CH_3O	H	C-C bond		H	H	H	2,6-Cl_2 Phenyl
9	H	H	H	H		"	"	"	"	"
10	H	CH_3O	CH_3O	H		"	"	"	"	2,6-F_2 Phenyl
11	H	H	H	H		"	"	"	"	"
12	H	CH_3O	CH_3O	H		"	"	"	"	2-I Phenyl
13	H	CH_3O	CH_3O	H		"	"	"	"	2,6-Cl_2 Phenyl
14	H	H	CH_3O	H		"	"	"	"	2-I Phenyl
15	H	H	CH_3O	H		"	"	"	"	2,6-F_2 Phenyl
16	H	CH_3O	CH_3O	H		"	"	"	"	2-F Phenyl
17	H	H	H	H		"	"	"	"	2-I Phenyl
18	H	CH_3O	CH_3O	H		"	"	"	"	2-Br Phenyl
19	H	Cl	H	H		"	"	"	"	2-Cl Phenyl
20	H	H	CH_3	H		"	"	"	"	"
21 (N-methyl iodide)	H	CH_3O	CH_3O	H		"	"	"	"	2,6 Cl_2 Phenyl
22	H	CH_3O	CH_3O	H		"	"	"	"	2,6-$(CH_3O)_2$ Phenyl

TABLE I (continued)

Example No.	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	A
23	H	H	Br	H	C-C bond		H	H	H	2-Cl Phenyl
24	H	CH_3O	CH_3O	H		"	"	"	"	2-CF_3 Phenyl
25	H	H	H	CH_3O		"	"	"	"	2,6-Cl_2 Phenyl
26	H	CH_3O	H	H		"	"	"	"	"
27	H	CH_3O	CH_3O	H		"	"	"	"	2-(Phenyl)Phenyl
28	H	CH_3O	CH_3O	H		"	"	"	"	2-(Phenoxy)Phenyl
29	H	CH_3O	CH_3O	H		"	C_2H_5	"	"	2,6-Cl_2 Phenyl
30	H	CH_3O	CH_3O	H		"	"	"	"	2,6-F_2 Phenyl
31	H	CH_3O	CH_3O	H		"	H	"	"	2-Cl Phenyl
32	H	CH_3O	CH_3O	H		"	"	"	"	2-Cl,6-F Phenyl
33	H	CH_3O	CH_3O	H		"	"	"	"	2,3,4-$(CH_3O)_3$-Phenyl
34	H	CH_3O	CH_3O	H		"	"	"	"	2-Cl,5-Br Phenyl
35	H	CH_3O	CH_3O	H		"	"	"	"	2-Cl,4-NO_2 Phenyl
36	H	CH_3O	CH_3O	H		"	"	"	"	3-F Phenyl
37	H	H	H	H		"	"	"	"	3-F Phenyl
38	H	CH_3O	CH_3O	H		"	"	"	"	3-Br Phenyl

TABLE I (continued)

Example No.	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	A
39	H	H	H	H	C-C bond		H	H	H	3-Br Phenyl
40	H	CH_3O	CH_3O	H	"		"	"	"	3,5-Cl_2 Phenyl
41	H	CH_3O	CH_3O	H	"		"	"	"	3-Cl Phenyl
42	H	H	H	H	"		"	"	"	"
43	H	CH_3O	CH_3O	H	"		"	"	"	3-CF_3 Phenyl
44	H	H	CH_3O	H	"		"	"	"	3-F Phenyl
45	H	CH_3O	CH_3O	H	"		"	"	"	4-SO_2CH_3 Phenyl
46	H	CH_3O	CH_3O	H	"		"	"	"	4-NO_2 Phenyl
47	H	CH_3O	CH_3O	H	"		"	"	"	4-CH_3 Phenyl
48	H	CH_3O	CH_3O	H	"		"	"	"	4-F Phenyl
49	CH_3O	H	H	H	"		"	"	"	"
50	H	H	CH_3	H	"		"	"	"	"
51	H	Cl	H	H	"		"	"	"	"
52	H	CH_3O	CH_3O	H	"		"	"	"	Phenyl
53	H	CH_3O	CH_3O	H	"		C_2H_5	"	"	4-F Phenyl
54	H	CH_3O	CH_3O	H	Cl	H	H	"	"	2-Cl Phenyl
55	H	$-OCH_2O-$		H	C-C bond		"	"	"	2,6-F_2 Phenyl

TABLE I (continued)

Example No.	R^1	R^2	R^3	R^4	R^5 R^6	R^7	R^8	R^9	A
56	H	CH_3O	CH_3O	H	C-C bond	H	H	H	2-OH Phenyl
57	H	$-OCH_2O-$		H	"	"	"	"	2,6-Cl_2 Phenyl
58	H	CH_3O	C_2H_5O	H	"	"	"	"	"
59	H	CH_3O	CH_3O	H	"	"	"	"	2-CH_3O Phenyl
60	H	CH_3O	CH_3O	H	"	"	"	"	2-NO_2 Phenyl
61	H	CH_3O	OH	H	"	"	"	"	2,6-Cl_2 Phenyl
62	H	OH	CH_3O	H	"	"	"	"	"
63	H	CH_3O	OH	H	"	"	"	"	2-CH_3 Phenyl
64	H	CH_3O	CH_3O	H	"	"	"	"	2-NH_2 Phenyl
65	H	C_3H_7O	CH_3O	H	"	"	"	"	2,6-Cl_2 Phenyl
66	H	C_3H_7O	CH_3O	H	"	"	"	"	2,6-F_2 Phenyl
67	H	CH_3O	C_2H_5O	H	"	"	"	"	"
68	H	C_2H_5O	CH_3O	H	"	"	"	"	2,6-Cl_2 Phenyl
69	H	C_2H_5O	CH_3O	H	"	"	"	"	2,6-F_2 Phenyl
70	H	CH_3O	$(CH_3)_2CHO$	H	"	"	"	"	2,6-Cl_2 Phenyl
71	H	CH_3O	$(CH_3)_2CHO$	H	"	"	"	"	2,6-F_2 Phenyl
72	H	CH_3O	C_3H_7O	H	"	"	"	"	2,6-Cl_2 Phenyl

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TABLE I (continued)

Example No.	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	A
73	H	CH_3O	C_3H_7O	H	C-C bond		H	H	H	2,6-F_2 Phenyl
74	H	CH_3O	C_4H_9O	H		"	"	"	"	2,6-Cl_2 Phenyl
75	H	CH_3O	C_4H_9O	H		"	"	"	"	2,6-F_2 Phenyl
76	H	CH_3O	$(CH_3)_2CHCH_2O$	H		"	"	"	"	2,6-Cl_2 Phenyl
77	H	CH_3O	$C_6H_{11}O$	H		"	"	"	"	2,6-Cl_2 Phenyl
78	H	CH_3O	$(CH_3)_2CHCH_2CH_2O$	H		"	"	"	"	"
79	H	CH_3O	$CH_3OCH_2CH_2O$	H		"	"	"	"	"
80	CH_3O	CH_3O	H	H		"	"	C-C bond		2-Cl Phenyl
81	CH_3O	CH_3O	H	H		"	"	"		2-NH_2 Phenyl
82	CH_3O	CH_3O	H	H		"	"	"		2-CF_3 Phenyl
83	CH_3O	CH_3O	H	H		"	"	"		2,6-$(CH_3O)_2$ Phenyl
84	CH_3O	CH_3O	H	H		"	"	"		2,3-$(CH_3O)_2$ Phenyl
85	CH_3O	CH_3O	H	H		"	"	"		2-Cl,4-NO_2 Phenyl
86	CH_3O	CH_3O	H	H		"	"	"		2-CH_3,3-NO_2 Phenyl
87	CH_3O	CH_3O	H	H		"	"	"		2-CH_3O Phenyl
88	CH_3O	CH_3O	H	H		"	"	"		2,4-F_2,3,5-Cl_2 Phenyl

TABLE I (continued)

Example No.	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	A
89	CH_3O	CH_3O	H	H	C-C bond		H	C-C bond		2-CH_3 Phenyl
90	CH_3O	CH_3O	H	H		"	"	"		2-Br Phenyl
91	CH_3O	CH_3O	H	H		"	"	"		2-F Phenyl
92	CH_3O	CH_3O	H	H		"	"	"		2-(2-Cl Pyrid-3-yl) Phenyl
93	CH_3O	CH_3O	H	H		"	"	"		2-Benzyl Phenyl
94	CH_3O	CH_3O	H	H		"	"	"		2,6-F_2 Phenyl
95	CH_3O	CH_3O	H	H		"	"	"		2,6-Cl_2 Phenyl
96	H	CH_3O	CH_3O	H		"	"	"		2,6-Cl_2 Phenyl
97	H	CH_3O	CH_3O	H		"	"	"		2,4-F_2,3,5-Cl_2 Phenyl
98	H	CH_3O	CH_3O	H		"	"	"		2-CH_3 Phenyl
99	H	CH_3O	CH_3O	H		"	"	"		2-Cl Phenyl
100	H	CH_3O	CH_3O	H		"	"	"		2,6-$(CH_3O)_2$ Phenyl
101	H	CH_3O	CH_3O	H		"	"	"		2-NO_2 Phenyl
102	H	CH_3O	CH_3O	H		"	"	"		2-CF_3 Phenyl
103	H	CH_3O	CH_3O	H		"	"	"		2,4-Cl_2 Phenyl

TABLE I (continued)

Example No.	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	A
104	H	CH_3O	CH_3O	H	C-C bond		H	C-C bond		2-(2-Cl Pyrid-3-yl) Phenyl
105	H	CH_3O	H	CH_3O		"	"	"		2,5-Cl_2,6-CH_3O Phenyl
106	H	CH_3O	H	CH_3O		"	"	"		2-NO_2 Phenyl
107	H	CH_3O	H	CH_3O		"	"	"		2-F Phenyl
108	H	CH_3O	H	CH_3O		"	"	"		2,4-F_2,3,5-Cl_2 Phenyl
109	H	CH_3O	H	CH_3O		"	"	"		2-CH_3 Phenyl
110	H	CH_3O	H	CH_3O		"	"	"		2,6-F_2 Phenyl
111	H	C_2H_5	C_3H_7	H		"	"	"		2,6-Cl_2 Phenyl
112	H	C_2H_5	C_3H_7	H		"	"	"		2-NO_2 Phenyl
113	H	CH_3O	C_2H_5O	H		"	"	"		2,6-Cl_2 Phenyl
114 (N-oxide)	H	CH_3O	CH_3O	H		"	"	H	H	2,4-Cl_2 Phenyl
115 (N-oxide)	H	CH_3O	CH_3O,	H		"	"	"	"	2-F,6-CF_3 Phenyl
116 (N-oxide)	H	CH_3O	CH_3O	H		"	"	"	"	2,6-Cl_2 Phenyl

TABLE I (continued)

Example No.	R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8	R^9	A
117 (N-oxide)	H	CH_3O	CH_3O	H	C-C bond		H	C-C bond		2,6-Cl_2 Phenyl
118 (N-oxide)	H	C_2H_5O	C_3H_7O	H	"		"	H	H	"
119 (N-oxide)	H	C_2H_5O	C_3H_7O	H	"		"	C-C bond		2-NO_2 Phenyl

TABLE IA

Ex. No.	M.pt. (°C)	^{1}H-NMR [ppm]
8	80	2.88(t,2H), 3.67(m,2H), 3.74(s,3H), 3.80(s,3H), 6.84(d,2H), 7.16-7.38 (m,4H)
9	95-98	2.90(m,2H), 3.97(m,2H), 6.89(d,1H), 7.17-7.43(m,6H)
10	135	2.81(t,2H), 3.72(s,3H), 3.96(m,5H), 6.52(s,1H), 6.77(s,1H), 7.00(t,2H), 7.38(m,1H)
11	oil	
12	oil	2.83(m,2H), 3.69(s,3H), 3.97(m,5H), 6.41(s,1H), 6.82(s,1H), 7.15(t,1H), 7.42(d,1H), 7.48(t,1H), 7.93(d,1H)
13	96	2.87(t,2H), 3.20(s,3H), 3.93(s,3H), 3.98(t,2H), 6.36(s,1H), 6.76(s,1H), 7.30(t,1H), 7.38(d,2H)
14	oil	2.81(t,2H), 3.72(s,3H), 3.82(t,2H), 6.42(d,1H), 6.93(dd,1H),7.10(t,1H), 7.18(d,1H), 7.37(t,1H), 7.42(t,1H), 7.86(d,1H)
15	oil	
16	124	2.79(t,2H), 3.72(s,3H), 3.88(t,2H), 3.95(s,3H), 6.60(s,1H), 6.77(s,1H), 7.14(t,1H), 7.23(t,1H), 7.43(m,1H), 7.52(t,1H)
17	108	2.85(t,2H), 3.95(m,2H), 6.86(d,1H), 7.05-7.30(m,3H), 7.35-7.50(m,3H), 7.89(d,1H)
18	100	2.92(m,2H), 3.63(s,3H), 3.97(m,5H), 6.40(s,1H), 6.81(s,1H), 7.30-7.50 (m,3H), 7.67(d,1H)
19	oil	2.89(m,2H), 3.80(m,2H), 6.83(d,1H), 7.17(dd,1H), 7.27(s,1H), 7.33-7.49 (m,4H)

TABLE IA (continued)

Ex. No.	M.pt. (°C)	^{1}H-NMR [ppm]
20	87	2.23(s,3H), 2.82(m,2H), 3.90(m,2H), 6.74(s,1H), 7.18(m,1H), 7.35-7.45 (m,5H)
21	semi-crystalline oil	
22	140	2.17(s,2H), 2.81(t,2H), 3.64(s,3H), 3.72(s,6H), 3.91(s,3H), 6.46(s,1H), 6.62(d,2H), 6.75(s,1H), 7.30(t,1H)
23		2.89(m,2H), 3.90(m,2H), 6.49(d,1H), 7.15-7.50(m,6H)
24	oil	2.80(t,2H), 3.62(s,3H), 3.90(m,5H), 6.32(s,1H), 6.77(s,1H), 7.43(d,1H), 7.58(m,2H), 7.74(d,1H)
25	169	2.81(t,2H), 3.42(s,3H), 3.90(t,2H), 6.76(d,1H), 6.89(d,1H), 7.20(dd,1H), 7.33(m,3H)
26	96	2.94(t,2H), 3.83(s,3H), 3.96(t,2H), 6.71(dd,1H), 6.82 (m,2H), 7.29 (dd,1H), 7.37(s,1H), 7.40(d,1H)
27	145	1.86(m,2H), 2.66(m,2H), 3.60(s,3H), 3.84(s,3H), 6.29(s,1H), 6.55(s,1H), 7.14(m,3H), 7.32(m,2H), 7.50(m,4H)
28	oil	2.43(m,2H), 3.76(s,3H), 3.96(m,5H), 6.65(m,4H), 6.96(t,1H), 7.03(d,1H), 7.18(t,2H), 7.29(t,1H), 7.43(t,1H), 7.56(d,1H)
29	116	1.09(t,3H), 1.70(m,2H), 1.96(m,1H), 2.70(dd,1H), 2.99(dd,1H), 3.67 (s,3H), 3.95(s,3H), 6.37(s,1H), 6.75(s,1H), 7.29(m,1H), 7.37(m,2H)
30	129	1.09(t,3H), 1.76(m,2H), 1.97(m,1H), 2.68(dd,1H), 2.94(dd,1H), 3.69(s,3H), 3.96(s,3H), 6.50(s,1H), 6.77(s,1H), 6.95(dd,2H), 7.38(m,1H)

TABLE IA (continued)

Ex. No.	M.pt. (°C)	^{1}H-NMR [ppm]
31	104	2.81(m,2H), 3.66(s,3H), 3.95(s,3H), 4.02(m,2H), 6.42(s,1H), 6.77(s,1H), 7.41(m,4H)
32	110	2.84(t,2H), 3.68(s,3H), 3.96(m,5H), 6.43(s,1H), 6.77(s,1H), 7.12(t,1H), 7.24(m,2H)
33	93	2.81(t,2H), 3.70(s,3H), 3.71(s,3H), 3.88(s,3H), 3.95(s,3H), 3.97(s,3H), 6.58(s,1H), 6.74(d+s,2H), 7.10(d,1H)
34	210 (de-comp.)	3.23(m,2H), 3.74(s,3H), 4.04(s,3H), 4.23(m,2H), 6.56(s,1H), 6.97(s,1H), 7.44(d,1H), 7.72(dd,1H), 7.80(d,1H)
35	190	2.83(m,2H), 3.66(s,3H), 3.97(s,3H), 4.05(m,2H), 6.32(s,1H), 6.78(s,1H), 7.65(d,1H), 8.22(dd,1H), 8.33(dd,1H)
36	128	2.78(t,2H), 3.77(s,3H), 3.82(m,2H), 3.97(s,3H), 6.80(d,2H), 7.14(m,1H), 7.40(m,3H)
37	oil	2.82(t,2H), 3.86(m,2H), 7.16(m,1H), 7.20-7.50(m,7H)
38	94	2.74(t,2H), 3.76(s,3H), 3.83(t,2H), 3.98(s,3H), 6.76(s,1H), 6.79(s,1H), 7.32(t,1H), 7.55(2d,2H), 7.81(s,1H)
39	oil	2.92(t,2H), 3.94(t,2H), 7.28(m,3H), 7.38(t,1H), 7.55(t,3H), 7.80(s,1H)
40	135	2.76(t,2H), 3.78(s,3H), 3.83(m,2H), 3.96(s,3H), 6.73(s,1H), 6.81(s,1H), 7.44(s,1H),7.55(s,2H)
41	112-114	2.76(t,2H), 3.76(s,3H), 3.83(m,2H), 3.96(s,3H), 6.75(s,1H), 6.88(s,1H), 7.32-7.51(m,3H), 7.64(s,1H)
42	100-103	

TABLE IA (continued)

Ex. No.	M.pt. (°C)	^{1}H-NMR [ppm]
43	oil	2.79(t,2H), 3.74(s,3H), 3.88(t,2H), 3.97(s,3H), 6.74(s,1H), 6.82(s,1H), 7.58(t,1H), 7.71(d,1H), 7.83(d,1H), 7.92(s,1H)
44	oil	2.77(t,2H), 3.75(s,3H), 3.85(t,2H), 6.82(d,1H), 6.98(dd,1H), 7.16(m,1H), 7.20(d,1H), 7.36(d,1H)
45	172	2.78(t,2H), 3.10(s,3H), 3.76(s,3H), 3.84(t,2H), 3.97(s,3H), 6.66(s,1H), 6.82(s,1H), 7.83(d,2H), 8.04(d,2H)
46	156	2.75(t,2H), 3.74(s,3H), 3.86(t,2H), 3.98(s,3H), 6.64(s,1H), 6.83(s,1H), 7.81(d,2H), 8.31(d,2H)
47	131	2.41(s,3H),2.74(t,2H), 3.76(s,3H), 3.80(m,2H), 3.96(s,3H), 6.78(s,1H), 6.83(s,1H), 7.22(d,2H), 7.51(d,2H)
48	125	2.76(t,2H), 3.76(s,3H), 3.81(m,2H), 3.96(s,3H), 6.77(s,1H), 6.79(s,1H), 7.10(t,2H), 7.62(dt,2H)
49	77	2.78(t,2H), 3.41(t,2H), 3.90(s,3H), 6.85(d,1H), 7.00(d,1H), 7.09(t,1H), 7.22(t,1H), 7.59(t,2H)
50	oil	2.31(s,3H), 2.78(t,2H), 3.83(t,2H), 7.02-7.25(m,5H), 7.61(m,2H)
51	semi-crystal-line oil	2.80(t,2H), 3.83(t, 2H), 7.05-7.35 (m,5H), 7.59(m,2H)
52	92	2.76(t,2H), 3.76(s,3H), 3.83(t,2H), 3.97(s,3H), 6.78(s,1H), 6.80(s,1H), 7.44(m,3H), 7.60(dd,2H)
53	119	1.14(t,3H), 1.70, 1.91(2xm,2H), 2.54 (dd,1H), 2.76(dd,1H), 3.38(m,1H), 3.75(s,3H), 3.96(s,3H), 6.74(s,1H), 6.79(s,1H), 7.12(t,2H), 7.61(m,2H)

TABLE IA (continued)

Ex. No.	M.pt. (°C)	^{1}H-NMR [ppm]
54	oil	2.86(m,2H), 3.03(m,2H), 3.70(s,3H), 3.89(s,3H), 5.58(s,1H), 6.26(s,1H), 6.65(s,1H), 6.96(dd,1H), 7.17(m,2H), 7.42(d,1H)
55	68	2.78(t,2H), 3.92(t,2H), 5.93(s,2H), 6.44(s,1H), 6.70(s,1H), 6.95(t,2H), 7.31(m,1H)
56	105	2.70(t,2H), 3.73(t,2H), 3.86(s,3H), 3.96(s,3H), 6.82(m,2H), 7.07(d,1H), 7.14(s,1H), 7.32(m,1H), 7.58(d,1H), 14.50(br s,1H)
57	108	2.78(t,2H), 3.92(t,2H), 5.93(s,2H), 6.31(s,1H), 6.74(s,1H), 7.27(t,1H), 7.31(m,1H)
58	92	1.31(t,3H), 2.33(t,2H), 3.47(q,2H), 3.90(s,3H), 6.35(s,1H); 6.74(s,1H), 7.30(d,1H), 7.37(d,2H)
59	100	
60	127	
61	234	
62	201	
63	142	
64	160	
65	105	
66	102	
67	91	1.38(t,3H), 2.84(t,2H), 3.95(m,5H), 6.56(s,1H), 6.77(s,1H), 7.01(t,2H), 7.38(m,1H)
68	99	

TABLE IA (continued)

Ex. No.	M.pt. (°C)	^{1}H-NMR [ppm]
69	90	
70	126	1.19(d,6H), 2.33(t,2H), 3.88(s,3H) 3.95(m,2H), 4.23(septet,1H), 6.39 (s,1H), 6.76(s,1H), 7.28(t,1H), 7.36 (d,2H)
71	123	1.23(d,6H), 2.80(t,2H), 3.88(s,3H), 3.92(t,2H), 4.25(septet,1H), 6.55(s,1H), 6.74(s,1H), 6.97(t,2H), 7.36(m,1H)
72	69	0.91(t,3H), 1.72(sextet,2H), 2.84 (t,2H), 3.74(t,2H), 3.90(s,3H), 3.94 (t,2H), 6.36(s,1H), 6.76(s,1H), 7.27(m,1H), 7.36(d,2H)
73	82	0.93(t,3H), 1.72(sextet,2H), 2.82 (t,2H), 3.76(t,2H), 3.90(s,3H), 3.94 (t,2H), 6.50(s,1H), 6.73(s,1H), 6.99 (t,2H), 7.37(m,1H)
74	oil	0.80(t,3H), 1.31(dq,2H), 1.63 (quintet,2H), 2.78(t,2H), 3.76(t,2H), 3.84(s,3H), 3.88(dd,2H), 6.30(s,1H), 6.71(s,1H), 7.22(t,1H), 7.32(d,2H)
75	80	0.88(t,3H), 1.37(dt,2H), 1.68(m,2H), 2.80(t,2H), 3.81(t,2H), 3.91(s,3H), 3.93(t,2H), 6.49(s,1H), 6.73(s,1H), 6.97(t,2H), 7.36(m,1H)
76	oil	0.82(d,6H), 1.91(m,1H), 2.73(t,2H), 3.44(d,2H), 3.78(s,3H), 3.84(t,2H), 6.24(s,1H), 6.66(s,1H), 7.28(d,1H), 7.27(d,2H)
77	oil	0.83(m,3H), 1.33(m,6H), 1.67(t,2H), 2.82(t,2H), 3.76(t,2H), 3.88(s,3H), 3.94(t,2H), 6.32(s,1H), 6.74(s,1H), 7.26(m,1H), 7.36(dd,2H)

TABLE IA (continued)

Ex. No.	M.pt. (°C)	^{1}H-NMR [ppm]
78	oil	0.81(d,6H), 1.57(quintet,2H), 1.64 (m,1H), 2.82(t,2H), 3.82(t,2H), 3.89 (s,3H), 3.92(m,2H), 6.34(s,1H), 6.74 (s,1H), 7.28(d,1H), 7.37(d,2H)
79	108	2.81(t,2H), 3.31(s,3H), 3.65(t,2H), 3.88(s,3H), 3.94(m,4H), 6.44(s,1H), 6.73(s,1H), 7.26(dd,1H), 7.35(d,2H)
80	83	4.00(s,3H), 4.01(s,3H), 7.35(m,6H), 7.94(d,1H), 8.55(d,1H)
81	85 (dec.)	4.02(s,6H), 6.82(d,2H), 7.27(m,3H), 7.77(d,1H), 7.88(d,1H), 8.50(d,1H)
82	114	4.00(s,3H), 4.02(s,3H), 7.24(m,2H), 7.40(d,1H), 7.62(m,2H), 7.32(dd,1H), 7.92(d,1H), 8.48(d,1H)
83	83	3.64(s,6H), 3.96(s,3H), 4.00(s,3H), 6.70(d,2H), 7.20(m,1H), 7.38(m,2H), 7.90(d,1H), 8.58(d,1H)
84	76	3.42(s,3H), 3.95(s,3H), 4.00(ds,6H), 7.02(m,2H), 7.24(m,2H), 7.54(dd,1H), 7.94(d,1H), 8.56(d,1H)
85	111	4.09(ds,6H), 7.30(s,2H), 7.65(d,1H), 8.05(d,1H), 8.28(dd,1H), 8.44(d,1H), 8.48(d,1H)
86	90-91	2.18(s,3H), 4.02(ds,6H), 7.25(m,2H), 7.48(m,2H), 7.95(m,2H), 8.56(d,1H)
87	120	3.71(s,3H), 4.00(ds,6H), 7.05(m,2H), 7.20(m,1H), 7.44(m,3H), 7.88(d,1H), 8.52(d,1H)
88	173-174	4.03(ds,6H), 7.35(d,1H), 7.55(m,2H), 7.98(d,1H), 8.55(d,1H)
89	74	4.03(s,3H), 7.28(m,6H), 7.88(d,1H), 8.52(d,1H)

TABLE IA (continued)

Ex. No.	M.pt. (°C)	^{1}H-NMR [ppm]
90	79	4.01(s,6H), 7.34(m,5H), 7.73(d,1H), 7.95(d,1H), 8.55(d,1H)
91	86-87	4.00(s,6H), 7.28(m,3H), 7.52(m,3H), 7.94(d,1H), 8.55(d,1H)
92	126-128	4.01(ds,6H), 7.32(m,3H), 7.84(dd,1H), 7.90(d,1H), 8.55(m,2H)
93	oil	3.83(d,2H), 3.98(s,3H), 4.02(s,3H), 7.16(m,11H), 7.90(d,1H), 8.55(d,1H)
94	oil	3.98(s,3H), 4.02(s,3H), 7.05(m,2H), 7.27(dd,1H), 7.45(m,2H), 7.97(d,1H), 8.58(d,1H)
95	108	4.00(s,3H), 4.04(s,3H), 7.29(s,2H), 7.48(m,3H), 7.95(d,1H), 8.56(d,1H)
96	152	3.81(s,3H), 4.06(s,3H), 6.69(s,1H), 7.16(s,1H), 7.38(dd,1H), 7.59(d,2H), 7.61(d,1H), 8.55(d,1H)
97	188	3.90(s,3H), 4.04(s,3H), 6.85(d,1H), 7.13(s,1H), 7.58(m,4H), 8.45(d,1H)
98	oil	2.06(s,3H), 3.76(s,3H), 4.02(s,3H), 6.83(s,1H), 7.11(s,1H), 7.32(d,1H), 8.46(d,1H)
99	oil	3.76(s,3H), 3.96(s,3H), 6.80(s,1H), 7.10(s,1H), 7.48(m,5H), 8.47(d,1H)
100	181-182	3.52(s,3H), 3.68(s,3H), 3.80(s,3H), 4.04(s,3H), 6.72(s,1H), 6.78(s,1H), 7.10(s,1H), 7.24(m,1H), 7.42(dd,1H), 7.50(d,1H), 8.45(d,1H)
101	184	3.78(s,3H), 4.04(s,3H), 6.84(d,1H), 7.13(s,1H), 7.64(m,4H), 8.15(d,1H)
102	81	3.70(s,3H), 3.97(s,3H), 6.64(s,1H), 7.07(s,1H), 7.50(m,4H), 7.77(d,1H), 8.42(d,1H)

TABLE IA (continued)

Ex. No.	M.pt. (°C)	^{1}H-NMR [ppm]
103	143	3.82(s,3H), 4.05(s,3H), 6.78(s,1H), 7.12(s,1H), 7.25(s,1H), 7.48(m,1H), 7.55(m,2H), 8.45(d,1H)
104	130	3.78(s,3H), 4.04(s,3H), 6.84(s,1H), 7.13(s,1H), 7.64(m,4H), 8.15(s,1H), 8.44(d,1H)
105	oil	3.53(s,6H), 3.83(s,3H), 6.45(d,1H), 6.73(d,1H), 7.15(d,1H), 7.35(d,1H), 7.52(d,1H), 8.50(d,1H)
106	oil	3.46(s,3H), 3.93(s,3H), 6.40(d,1H), 6.75(d,1H), 7.50(m,4H), 8.13(d,1H), 8.45(d,1H)
107	oil	3.54(s,3H), 3.92(s,3H), 6.48(d,1H), 6.70(d,1H), 7.14(m,1H), 7.40(m,3H), 7.60(d,1H), 8.47(d,1H)
108	oil	3.53(s,3H), 3.90(s,3H), 6.50(d,1H), 6.70(d,1H), 7.44(dd,1H), 7.50(d,1H), 8.92(d,1H)
109	oil	1.96(s,3H), 3.46(s,3H), 3.90(s,3H), 6.40(d,1H), 6.23(d,1H), 7.18(m,4H), 7.43(d,1H), 8.44(d,1H)
110	oil	3.46(s,3H), 3.84(s,3H), 6.48(d,1H), 6.94(m,3H), 7.32(m,1H), 7.56(d,1H), 8.33(d,1H)
111		0.97(t,3H), 1.48(t,3H), 1.80(m,2H), 4.20(q,2H), 4.84(t,2H), 6.62(s,1H), 7.12(s,1H), 7.37(m,3H), 7.52(d,1H), 8.46(d,1H)
112	80-82	1.00(t,3H), 1.55(t,3H), 1.82(m,2H), 3.86(q,2H), 4.23(q,2H), 7.06(s,1H), 7.62(m,4H), 7.77(s,1H), 8.14(d,1H), 8.38(d,1H)
113	145	1.40(t,3H), 3.98(q,2H), 4.01(s,3H), 6.65(s,1H), 7.14(s,1H), 7.36(dd,1H), 7.47(dd,2H), 7.59(d,1H), 8.50(d,1H)

TABLE IA (continued)

Ex. No.	M.pt. (°C)	^1H-NMR [ppm]
114	178	3.1-3.32(m,2H), 3.66(s,3H), 3.90 (s,3H), 4.20-4.34(m,2H), 6.12(s,1H), 6.78(s,1H)), 7.28-7.61(m,3H)
115	80-83	3.1-3.3(m,2H), 3.62(s,3H), 3.9(s,3H), 4.2-4.35(m,2H), 6.08(s,1H), 6.80 (s,1H), 7.46-7.7(2m,3H)
116	166-168	3.24(m,2H), 3.64(s,3H), 3.93(s,3H), 4.29(m,2H), 6.10(s,1H), 6.80(s,1H), 7.35-7.48(m,3H)
117	210-211	3.75(s,3H), 4.04(s,3H), 6.35(s,1H), 7.13(s,1H), 7.38-7.52(mm,3H), 7.53 (d,1H), 8.28(d,1H)
118	110-111	1.0(t,3H), 1.47(t,3H), 1.70(m,3H), 3.24(m,2H), 3.75(m,2H), 4.14(q,2H), 4.30(q,2H), 6.10(s,1H), 6.78(s,1H), 7.3-7.5(m,3H)
119	oil	1.0(t,3H), 1.54(t,3H), 1.7-1.85 (m,2H), 3.8(m,2H), 4.2(m,2H), 6.50 (s,1H), 7.13(s,1H), 7.45-7.9(m,4H), 8.27(d,1H), 8.36(d,1H)

EXAMPLE 120

Biological activity against powdery mildew

The compounds were tested for activity against powdery mildew on cucumber, barley and wheat. The phytopathogenic fungi tested were:

EG_b: *Erysiphe graminis* f.sp. *hordei* barley-Golden Promise

EG_w: *Erysiphe graminis* f.sp. *tritici* wheat-Kormoran

EC : *Erysiphe cichoracearum* cucumber-Hokus

EG_b and EG_w:

The test plants were cultivated in 6cm diameter pots filled with Fruhstorfer Erde Typ N (Industrie-Erden-Weke Erich Archut, D-6420 Lauterbach-Wallenrod, West Germany). Seven seeds were sown in each pot. The test plants were grown for 1 week to the one-leaf stage at a temperature of 23°C during the day and 18°C at night.

The test compounds were dissolved in either acetone or methanol, depending on their solubility, to a final concentration of 5000ppm. Triton X 150 (5000ppm) was added as emulgator. The resulting mixture was diluted with deionised water to a concentration of 400ppm of active ingredient (a.i.). Two pots with seven plants each were sprayed to run off in a spray cabin with spray wash (20ml). After drying of the spray film in a hood, the plants were placed in a greenhouse at 20°-25°C.

One day after applying the test compounds to the plants, stock plants with strongly sporulating Erysiphe fungi were shaken over the test plants until the leafs were clearly visibly dusted with mildew spores. For about 3 hours, air movement was reduced as far as possible by closing doors and windows and by switching off the lighting. The plants were kept in the greenhouse until the symptoms had developed.

The assessment was carried out about 1 week after infection using the following scale:

1° = whole plant without infestation
1 = infestation up to 10% of leaf area
2 = 11-40% infestation
3 = ≤41% infestation

P denotes phytotoxicity

EC:

The test plants were sown in plant-trays and, as soon as the cotyledons were exposed, they were transferred to 6cm diameter pots filled with Fruhstorfer Erde Typ N. The test plants were grown for 1 week to treatment stage at a temperature of 23°C during the day and 18°C at night.

The test compounds were dissolved in either acetone or methanol, depending on their solubility, to a final concentration of 5000ppm. Triton X 150 (5000ppm) was added as emulgator. The resulting mixture was diluted with deionised water to a concentration of 400ppm of active ingredient (a.i.). Two pots with one plant each were sprayed to run off in a spray cabin with spray wash (20ml). After drying of the spray film in a hood, the plants were placed in a greenhouse at 20°-25°C.

One day after applying the test compounds to the plants, stock plants (variety Hoffmanns Produkta) with strongly sporulating Erysiphe fungi were treated with an air jet over the test plants until the leafs were clearly visibly dusted with mildew spores. For about 3 hours, air movement was reduced as far as possible by closing doors and windows and by switching off the lighting. The plants were kept in the greenhouse until the symptoms had developed.

The assessment was carried out about 1 week after infection using the scale described above.

The results of these tests are set out in Table II below:-

TABLE II

Example No.	Assessment EC	Assessment EG_b	Assessment EG_w
1	2	2	3
3	0	3^p	3^p
4	2^p	2^p	2^p
5	-	-	1
8	3^p	-	-
9	3^p	3^p	3^p
10	3^p	1^p	1^p
11	3	2	3
12	3	1^p	1^p
13	3	1	1
14	3	2^p	2^p
15	3	3	3
16	3	2	3
17	3	3^p	3^p
18	3	1^p	1^p
19	3	3	3
20	2^p	3^p	3^p
21	3^p	3^p	3^p
22	3	3	3
23	3	3	3
24	3^p	1^p	1^p
25	3	1^p	1^p
26	2	1	1
27	3	1	1
28	3	3	3
33	3^p	2^p	3^p
34	3	2	3
35	3	3^p	3^p
36	3	2^p	2^p

TABLE II (continued)

^{p} denotes phytox

Example No.	Assessment EC	EG_b	EG_w
37	3^p	2^p	2^p
38	3	3	3
39	3	3^p	3^p
40	3	2	3
41	3	3	3
42	3	3	3
43	3	1	2
44	3^p	2^p	3^p
45	3	3	3
46	3	3	3
47	3	3	3
48	3	3	3
49	2	3	3
50	3^p	3^p	3^p
51	3	2	3
52	3	3^p	3^p
53	3	3	3
58	1^p	1^p	1^p
59	3	3	3
60	3^p	3^p	3^p
61	3	3	3
62	3^p	3^p	3^p
63	2	3^p	3^p
64	2	3^p	3^p
67	3^p	3^p	3^p
70	1^p	1^p	1^p
71	3	1^p	1^p
72	-	1^p	1^p
73	2	1^p	1^p
74	1^p	1^p	1^p

TABLE II (continued)

^{P} denotes phytox

Example No.	Assessment EC	EG_b	EG_w
75	1	1^P	1^P
80	3^P	2^P	3^P
81	1^P	3^P	3^P
82	2^P	2^P	2^P
83	3^P	3^P	3^P
84	3^P	3^P	3^P
85	3^P	3^P	3^P
86	1^P	2^P	2^P
87	1	2^P	3^P
88	1^P	0	3^P
89	3^P	3^P	2^P
90	2^P	2^P	2^P
91	2^P	3^P	3^P
92	2^P	3^P	3^P
93	3^P	3^P	3^P
94	3^P	2^P	2^P
95	2	3	3
96	1	1^P	1^P
97	1	3^P	3^P
98	3	1	1
99	1^P	1^P	1^P
100	3^P	3^P	3^P
101	1^P	1^P	1^P
102	2^P	1^P	1^P
103	1^P	1^P	1^P
104	1^P	2^P	2^P
113	0	0	0

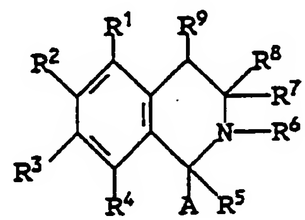
In further tests, the residual (R) and curative (C) activities of various compounds against powdery mildew in barley and wheat was determined at various concentrations of the test compounds. The results, expressed as % activity, are given in Table III below:-

TABLE III

Ex. No.		Barley Concentration (ppm)	Barley Activity (%)	Wheat Concentration (ppm)	Wheat Activity (%)
6	R	100	100	400	98.8
	C	100	100	400	68.5
7	R	400	75	400	94
	C	100	100	400	23
117	R	100	100	100	100
	C	100	100	400	100
118	R	100	100	100	100
	C	100	100	400	100
119	R	400	30	400	80
	C	400	99	400	30

CLAIMS

1. A method of combating fungus at a locus which comprises treating the locus with a compound of the general formula



(I)

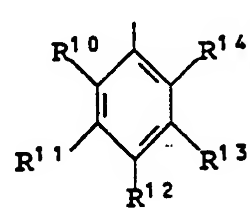
or an N-alkyl or N-phenyl halide or N-oxide thereof, in which
R^1, R^2, R^3 and R^4 independently represent a hydrogen or halogen atom, a hydroxyl group or an optionally substituted alkyl or alkoxy group, or R^1 and R^2 or R^2 and R^3 or R^3 and R^4 together with the interjacent carbon atoms represent a 5- to 7-membered saturated or unsaturated carbocyclic or heterocyclic ring in which a heterocyclic ring contains 1 to 3 heteroatoms selected from nitrogen, oxygen and sulphur atoms;
R^5 represents a hydrogen or halogen atom,
R^6 represents a hydrogen atom, or

R^5 and R^6 together represent a single carbon-carbon bond;
R^7 represents a hydrogen or halogen atom, an alkyl or alkoxy group optionally substituted by one or more halogen atoms, or an optionally substituted phenyl or phenoxy group;
R^8 and R^9 independently represent a hydrogen atom or together represent a single carbon-carbon bond; and
A represents an optionally substituted phenyl group.

2. A method according to claim 1 in which R^1, R^2, R^3 and R^4 independently represent a hydrogen or halogen atom, a hydroxyl group or a C_{1-6} alkyl or C_{1-6} alkoxy group each optionally substituted by one or more halogen atoms or C_{1-4} alkoxy groups, or R^1 and R^2 or R^2 and R^3 or R^3 and R^4 together with the interjacent carbon atoms represents a 5- or 6-membered saturated heterocyclic ring containing two oxygen atoms.

3. A method according to claim 1 or claim 2 in which R^7 represents a hydrogen atom or a C_{1-6} alkyl group.

4. A method according to any one of the preceding claims in which A represents a group



in which

R^{10}, R^{11}, R^{12}, R^{13} and R^{14} independently represent a hydrogen or halogen atom, a hydroxyl, nitro or amino group, or an optionally substituted alkyl, alkoxy, alkylamino, dialkylamino, alkylthio, alkylsulphinyl, alkylsulphonyl, aralkyl, phenyl, phenoxy or pyridyl group.

5. A method according to claim 4 in which R^{10}, R^{11}, R^{12}, R^{13} and R^{14} independently represent a hydrogen or halogen atom, a hydroxyl, nitro or amino group, or an alkyl, alkoxy, alkylsulphonyl, benzyl, phenyl, phenoxy or pyridyl group each optionally substituted by one or more halogen atoms.

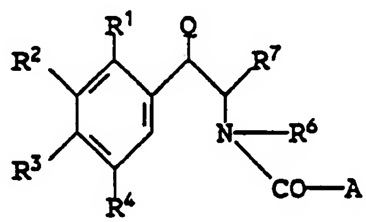
6. A method according to claim 4 or claim 5 in which R^1, R^2, R^3 and R^4 independently represent a hydrogen, chlorine or bromine atom or a hydroxyl, methyl, ethyl, propyl, methoxy, ethoxy, propoxy, butoxy, pentyloxy, hexyloxy or methoxyethoxy group, or R^2 and R^3 together with the interjacent carbon atoms represent a 1,3-dioxolane ring; R^5 represents a hydrogen or chlorine atom, R^6 represents a hydrogen atom, or R^5 and R^6 together represent a single carbon-carbon bond; R^7 represents a hydrogen atom or an ethyl group; and R^{10}, R^{11}, R^{12}, R^{13} and R^{14} independently represent a hydrogen, fluorine, chlorine, bromine or iodine atom or a hydroxyl, nitro, amino, methyl, trifluoromethyl, methoxy, methylsulphonyl, benzyl, phenyl, phenoxy or chloropyridyl group.

7. The use as a fungicide of a compound of formula I, or an N-alkyl or N-phenyl halide or N-oxide thereof, as defined in any one of the preceding claims.

8. A compound of the general formula I as defined in claim 1 with the proviso that, when R^1, R^4, R^5, R^6, R^7, R^8 and R^9, all represent a hydrogen atom and A represents a 3,4,5-trimethoxyphenyl group, then R^2 and R^3 together with the interjacent carbon atoms do not represent a 1,3-dioxolane ring.

9. A process for the preparation of a compound of formula I as defined in claim 8 (or an N-alkyl or N-phenyl halide) or N-oxide thereof which comprises

(a) cyclising a compound of the general formula



(II)

in which R^1, R^2, R^3, R^4, R^6, R^7 and A are as defined in claim 8 and, when R^8 and R^9 in the resultant compound of formula I both represent a hydrogen atom then Q represents a hydrogen atom, and, when R^8 and R^9 in the resultant compound of formula I together represent a single carbon-carbon bond then Q represents an alkoxy group, in the presence of a dehydrating agent to form a compound of formula I in which R^5 and R^6 together represent a single carbon-carbon bond; followed, if desired, when R^8 and R^9 both represent a hydrogen atom, by

(b) hydrogenating the resulting compound of formula I to produce a compound of formula I

in which R^5, R^6, R^8 and R^9 all represent a hydrogen atom; or

(c) dehydrogenating the resulting compound of formula I to produce a compound of formula I in which R^5 and R^6 together and R^8 and R^9 together both represent a single carbon-carbon bond;

followed, if desired by,

(d) oxidising the compound of formula I formed in (a), (b) or (c) to form an N-oxide thereof; or

(e) converting the compound of formula I formed in (a), (b) or (c) to the corresponding N-alkyl or N-phenyl halide.

10. A fungicidal composition which comprises a carrier and, as active ingredient, a compound of the general formula I as defined in claim 8.

INTERNATIONAL SEARCH REPORT

International Application No PCT/EP 91/02444

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl.5 C 07 D 217/16 C 07 D 217/14 C 07 D 217/22
C 07 D 491/04 A 01 N 43/42 //(C 07 D 491/04 C 07 D 317:00)

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl.5	C 07 D A 01 N

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category °	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	DE,A,3900233 (SANDOZ-PATENT-GmbH) 20 July 1989, see claims 1-4 ---	8,9
X	EP,A,0251361 (DUPHAR INTERNATIONAL RESEARCH B.V.) 7 January 1988, see claims 1,2 (cited in the application) ---	8,9
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X	FR,A,2238489 (G.D. SEARLE AND CO.) 21 February 1975, see page 9; example 6 ---	8,9
X	GB,A,1176804 (Dr. KARL THOMAE GmbH) 7 January 1970, see claims --- -/-	8,9

° Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
03-03-1992	-7. 04. 92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	Maria Peis Maria Paz

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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

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A	EP,A,0121753 (HOECHST AG) 17 October 1984, see pages 26-28; claim 1 (cited in the application) -----	1,8,9

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. EP 9102444 SA 54274

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 31/03/92. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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FR-A- 760825		None	
GB-A- 645139		None	

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